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Tanaka

DERWENT-ACC-NO: 1993-390183
DERWENT-WEEK: 199349

TITLE: Cleaning substrate surface - by applying vapour of sulphuric acid anhydride to substrate surface, and removing obtd. sulphate using pure water NoAbstract

PRIORITY-DATA: 1992JP-0118066 (April 10, 1992)

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PATENT-FAMILY:

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INT-CL (IPC): H01L 21/302; H01L 21/304

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TITLE: CLEANING METHOD FOR SUBSTRATE SURFACE

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INVENTOR-INFORMATION:

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APPL-NO: JP04118066

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ABSTRACT:

PURPOSE: To selectively **remove** a metal oxide film by a method wherein the steam of **anhydrous sulfuric** acid is supplied to the surface of a substrate and the metal oxide film which has been applied to the surface of the substrate so as to be thin film-shaped is reacted with the **anhydrous sulfuric** acid.

CONSTITUTION: The steam of anhydrous sulfuric acid is introduced into a chamber 10 through a steam pipe 20 by means of an inert carrier gas from a steam supply device 18. The steam of the anhydrous sulfuric acid is supplied to the surface of a wafer which is provided with a metal electrode interconnection. By this treatment, an aluminum spontaneous oxide film with which the surface of a metal layer forming the metal electrode interconnection on the wafer, e.g. an aluminum layer, has been covered is corroded by the anhydrous sulfuric acid; aluminum sulfate is produced by a direct reaction at this time. Thereby, only the aluminum spontaneous oxide film on the surface can be corroded.

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	351	Z 8728－4M		

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(54)【発明の名称】　基板表面の洗浄方法

(57)【要約】
【目的】　金属層の表面に形成された金属自然酸化膜を、金属層を腐食させずに選択的に除去し、清浄な金属層表面が得られるようにする。
【構成】　無水硫酸の蒸気を基板の表面に供給し、基板上の金属層表面に形成された金属自然酸化膜に無水硫酸を反応させて硫酸塩を生成させる。基板表面に溶存酸素を殆んど含まない純水を供給し、純水で硫酸塩を溶解除去した後、不活性ガス雰囲気下で基板表面を乾燥させる。

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【特許請求の範囲】

【請求項1】　基板の表面に無水硫酸の蒸気を供給し、基板表面に薄膜状に被着した金属酸化物と無水硫酸とを反応させて硫酸塩を生成させる工程と、基板の表面に純水を供給し、基板表面に付着した硫酸塩を溶解させて基板表面から除去する工程と、硫酸塩が溶解除去された後の基板の表面を乾燥させる工程とからなる基板表面の洗浄方法。

【請求項2】　不活性ガス雰囲気内において少なくとも前記乾燥工程を行なう請求項1記載の基板表面の洗浄方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】この発明は、半導体デバイスや電子デバイスなどの製造工程において、基板上の金属層の表面に形成された金属自然酸化膜を基板上から除去する基板表面の洗浄方法に関する。

【0002】

【従来の技術】半導体デバイスや電子デバイスにおいて、素子からの電気信号を伝送したり取り出したりする電極と半導体素子本体又は他の電極配線との接触部分はコンタクト部と呼ばれ、それらは基板上の絶縁膜に形成されたコンタクトホールやスルーホールを介して電気的に接続している。このコンタクト部には、電流－電圧特性が直線的な関係となるオーミック性、低コンタクト抵抗性、界面安定性、良好な密着性などが要求される。ところで、半導体デバイスや電子デバイスの製造工程において、基板上に形成された金属層の表面には、空気中において容易に自然酸化膜が形成され成長する。例えば、室温におけるアルミニウムの自然酸化膜の飽和膜厚は3ｎｍである、といった報告がなされている。

【0003】半導体素子や下層電極配線或いはスルーホールやコンタクトホールの金属表面が自然酸化膜によって被覆されたままになっていると、デバイスにおけるコンタクト抵抗が増大する他、上記諸要求が満たされなくなる。さらに、半導体デバイスや電子デバイスの製造過程で金属層の表面に自然酸化膜が形成されていると、金属のエッチング反応が阻害され、不均一処理の原因となる。従って、半導体デバイスや電子デバイスの製造工程の各段階において、金属層の表面に自然酸化膜が形成されると、それを金属層表面から完全に除去しておく必要がある。従来、金属層の表面に形成された金属自然酸化膜は、腐食性ガスを使用してドライ洗浄により除去されていた。

【0004】

【発明が解決しようとする課題】しかしながら、シリコン層表面に形成されたシリコン自然酸化膜の除去は、フッ酸系液やその蒸気によって簡単に除去することができる（特表昭62－502930号公報等参照）が、金属層表面に形成された金属自然酸化膜の除去は非常に困難

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であり、ドライ洗浄により金属自然酸化膜を除去する上記方法も、プロセスの制御が困難であって自然酸化膜だけを選択的に除去することができず、また処理コストが高価であり、基板のダメージ、基板上への反応成分分子の吸着等といった問題点がある。このように、金属層表面から金属自然酸化膜を除去する有効な方法は、未だ見付かっていないのが現状である。

【0005】この発明は、以上のような事情に鑑みてなされたものであり、金属層の表面に形成された金属自然酸化膜を、金属層まで腐食させたりすることなく選択的に除去することができ、基板上への不純物や反応生成物の付着等といったことも起こらない基板表面の洗浄方法を提供することを目的とする。

【0006】

【課題を解決するための手段】この発明では、腐食薬剤として無水硫酸を使用し、その無水硫酸の蒸気を基板の表面に供給し、基板表面に薄膜状に被着した金属酸化物と無水硫酸とを反応させて硫酸塩を生成させるようにした。続いて、基板の表面に純水を供給し、基板表面に付着した硫酸塩を溶解させて基板表面から除去し、その後に、基板表面を乾燥させるようにした。以上の各工程、特に乾燥工程は、不活性ガス雰囲気内において行なうようにすることが望ましく、また、基板表面に供給する純水として、溶存酸素が殆んど含まれていない純水を使用することが好ましい。

【0007】ここで、金属層の表面が金属酸化膜で被覆された基板に、水を含んだ硫酸を接触させた場合には、表面の金属酸化膜だけでなく、その下の金属層まで硫酸によって腐食されてしまう。これに対し、この発明の方法では、基板の表面に無水硫酸の蒸気を供給するようにしているので、表面の金属酸化物のみと無水硫酸が反応し、金属酸化膜だけが腐食されて、その下の金属層は腐食されない。また、基板がダメージを受けることもない。そして、金属酸化物（M_2O_3）と無水硫酸（SO_3）とが直接に反応することにより、化1に示すように硫酸塩（$M_2(SO_4)_3$）が生成する。

【0008】

【化1】

$$M_2O_3 + 3SO_3 \longrightarrow M_2(SO_4)_3$$

【0009】金属酸化物と無水硫酸との反応によって生成した硫酸塩は、水に溶解され易く、基板表面に純水が供給されることにより、硫酸塩は純水中に溶解して基板上から除去され、有機物等の不純物も純水によって基板表面から洗い流される。このとき、溶存酸素が殆んど含まれていない純水を使用し、そして、基板表面の乾燥処理を不活性ガス雰囲気内で行なうようにすれば、金属酸化膜が除去された金属層の表面が再び酸化作用を受けて、金属層表面に金属酸化膜が再形成されるといった心配が無くなる。

【0010】

【実施例】以下、この発明の好適な実施例について説明する。

【0011】図1は、この発明に係る基板表面洗浄方法を実施するのに使用される洗浄装置の構成の1例を示す概略断面図である。この洗浄装置は、開閉シャッタ14が配設されたウエハ搬出入口12を有するチャンバ10内に、ウエハを上面に載置して水平面内において回転する回転支持テーブル16を配設して構成されている。チャンバ10には、無水硫酸の蒸気供給装置18が蒸気配管20を介して連通接続されているとともに、窒素供給源がガス配管22を介して連通接続されている。また、チャンバ10の内部の回転支持テーブル16の上面の方向に噴射口が向けられた純水噴出パイプ24がチャンバ10に配設されており、純水噴出パイプ24には給水配管26を介して純水供給源が流路接続されている。また、チャンバ10の底部には、排液・排気口28が形成されている。

【0012】図1に示した装置を使用し、以下のようにして基板表面の洗浄処理が行なわれる。まず、基板、例えばメタル電極配線付ウエハをウエハ搬出入口12を通してチャンバ10内へ搬入し、その後に開閉シャッタ14によりウエハ搬出入口12を閉塞する。そして、チャンバ10内へ不活性ガス、例えば窒素ガスを窒素供給源からガス配管22を通して送り込み、以後、一連の洗浄処理が終了するまでチャンバ10内へ窒素ガスを送給し続け、チャンバ10内を酸素が存在しない不活性ガス雰囲気に保つ。この状態で無水硫酸の蒸気を蒸気供給装置18から不活性キャリアガス（窒素ガス）によって蒸気配管20を通しチャンバ10内へ導入し、メタル電極配線付ウエハの表面に無水硫酸の蒸気を供給する。この処理により、ウエハ上のメタル電極配線を形成する金属層、例えばアルミニウム層の表面を被覆しているアルミニウム自然酸化膜（Al_2O_3）が無水硫酸によって腐食され、そのときの直接反応によって化2に示すように硫酸アルミニウム（$Al_2(SO_4)_3$）が生成する。

【0013】

【化2】

$$Al_2O_3 + 3SO_3 \longrightarrow Al_2(SO_4)_3$$

【0014】この場合、一般にアルミニウムは無水硫酸に対する防食材料として選定されることからも知れるように、表面のアルミニウム自然酸化膜だけが腐食され、その下のアルミニウム層（電極配線）まで腐食されることはない。

【0015】次に、純水供給源から給水配管26を通し溶存酸素が殆んど含まれていない純水をチャンバ10へ供給し、純水噴出パイプ24から純水を回転支持テーブル16上に載置固定されているウエハの表面へ吹き付ける。この処理により、硫酸アルミニウムは純水中に溶解し（水に対する硫酸アルミニウムの溶解度は、107.4g／100gである）、ウエハ表面から流下する水と一緒に硫酸アルミニウムがウエハ上から除去される。また、このとき、ウエハ表面に付着していた有機物なども洗い流される。そして、廃液は、排液・排気口28から窒素ガスと一緒にチャンバ10外へ排出される。

【0016】最後に、チャンバ10内へ窒素ガスを供給し続けたまま、窒素ガス雰囲気下でウエハ表面を乾燥させ、乾燥処理が終了すると、ウエハをチャンバ10から搬出して、次の処理室、例えば金属成膜室或いはエッチング処理室へウエハを移送する。

【0017】図2は、この発明に係る基板表面洗浄方法を適用して金属自然酸化膜を除去する過程を説明するための図である。図2の（a）は、絶縁層30の表面に金属層、例えばアルミニウム層32が被着形成され、そのアルミニウム層32の表面にアルミニウム自然酸化膜34が形成されて、表面がアルミニウム自然酸化膜34で被覆されたアルミニウム層32上に、スルーホール38を有する絶縁膜36が被着形成されている状態を示している。この図2の（a）に示した状態のまま、絶縁膜36の表面及びスルーホール38内に2層目の金属層を形成すると、コンタクト抵抗の増大等といった不都合を生じるため、上記したこの発明に係る方法を用いて、アルミニウム自然酸化膜34の、スルーホール38の形成部分に対応する部分を除去する。それにより、図2の（b）に示すように、絶縁膜36のスルーホール38の底部に、アルミニウム自然酸化膜が除去され有機物等の不純物の付着も無いアルミニウム層32の表面が露出する。この状態にしてから、図2の（c）に示すように、絶縁膜36上に2層目のアルミニウム層40を形成することにより、1層目のアルミニウム層32と2層目のアルミニウム層40とがスルーホール38を介して直接に接続された基板が得られる。

【0018】また、図示していないが、絶縁基板の表面に被着形成された金属層、例えばアルミニウム層をエッチング処理する場合には、所要パターンのレジスト膜で被覆されたアルミニウム層の、レジスト膜で被覆されていない部分の表面に形成されたアルミニウム自然酸化膜を、上記したこの発明に係る方法を用いて除去した後、アルミニウム層の、レジスト膜で被覆されていない部分を食刻し、エッチング後にアルミニウム層上からレジスト膜を剥離するようにすればよい。このように自然酸化膜を除去してからアルミニウム層をエッチング処理することにより、エッチング処理を均一に行なうことができる。また、アルミニウム層上からレジスト膜を剥離した後、再度この発明に係る方法を利用して、アルミニウム層の表面の、レジスト膜で被覆されていた部分に残存しているアルミニウム自然酸化膜を除去しておくようにする。図3に、この発明に係る方法を利用した、デバイス製造工程の一部のフローチャートを示す。

【0019】

【発明の効果】この発明は以上説明したように構成されかつ作用するので、この発明に係る方法により基板の表

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面を洗浄するようにすれば、金属層を腐食させたりすることなくその表面に形成された金属自然酸化膜だけを選択的に除去して、有機物等の不純物や反応生成物の付着が無く金属自然酸化膜で被覆されていない清浄な金属層表面を得ることができ、洗浄の際に基板がダメージを受けることもなく、この発明は、半導体デバイスや電子デバイスの品質向上に大いに寄与し得るものである。

【図面の簡単な説明】

【図１】この発明に係る基板表面洗浄方法を実施するのに使用される洗浄装置の構成の１例を示す概略断面図である。

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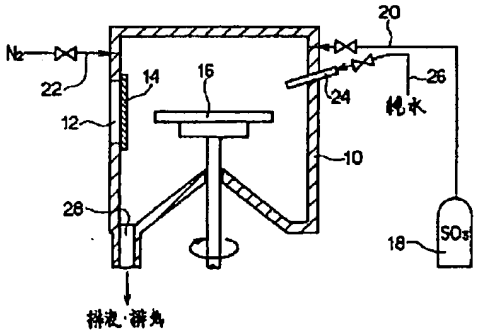
【図２】この発明に係る基板表面洗浄方法の適用例を説明するための基板の一部拡大縦断面図である。

【図３】この発明に係る基板表面洗浄方法を利用した、デバイス製造工程の一部の手順を示すフローチャートである。

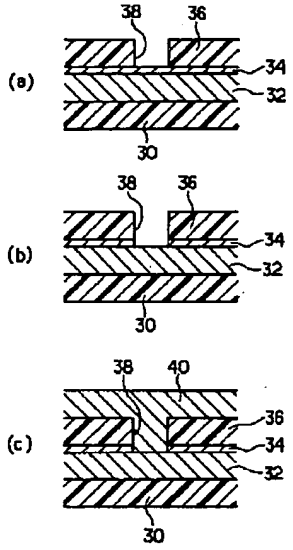
【符号の説明】

10　チャンバ
16　回転支持テーブル
18　無水硫酸の蒸気供給装置
22　窒素ガス配管
24　純水噴出パイプ

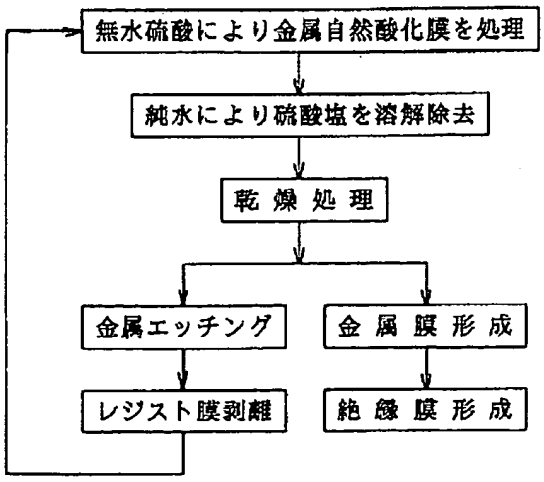
【図１】



【図２】



【図３】



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CLAIMS

[Claim(s)]
[Claim 1] The washing approach on the front face of a substrate which consists of the process which the steam of a sulfuric anhydride supplies [process] on the surface of a substrate, makes the metallic oxide and the sulfuric anhydride put on the substrate front face in the shape of a thin film react, and makes a sulfate generate, a process which supplies pure water to the front face of a substrate, make dissolve the sulfate adhering to a substrate front face, and remove from a substrate front face, and a process which dry the front face of the substrate after dissolution removal of the sulfate was carried out.
[Claim 2] The washing approach on the front face of a substrate according to claim 1 of performing said desiccation process at least in an inert gas ambient atmosphere.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the washing approach on the front face of a substrate of removing the metal natural oxidation film formed in the front face of the metal layer on a substrate from on a substrate, in production processes, such as a semiconductor device and an electron device.
[0002]
[Description of the Prior Art] In a semiconductor device or an electron device, the contact part with the electrode, the semiconductor device body, or other electrode wiring which transmit or take out the electrical signal from a component was called the contact section, and they are electrically connected through the contact hole and through hole which were formed in the insulator layer on a substrate. The ohmic nature from which the current-voltage characteristic serves as linear relation, low contact resistance, interface stability, good adhesion, etc. are required of this contact section. By the way, in the production process of a semiconductor device or an electron device, the natural oxidation film is easily formed into air, and it grows up to be the front face of the metal layer formed on the substrate. For example, the report that the saturation thickness of the natural oxidation film of the aluminum in a room temperature is 3nm is made.
[0003] Many above-mentioned demands are no longer filled except that the contact resistance in a device will increase, if the surface of metal of a semiconductor device, lower layer electrode wiring or a through hole, or a contact hole remains covered with the natural oxidation film. Furthermore, if the natural oxidation film is formed in the front face of a metal layer in the manufacture process of a semiconductor device or an electron device, a metaled etching reaction will be checked and it will become the cause of ununiformity processing. Therefore, in each phase of the production process of a semiconductor device or an electron device, if the natural oxidation film is formed in the front face of a metal layer, it is necessary to remove it completely from a metal layer front face. Conventionally, the metal natural oxidation film formed in the front face of a metal layer was removed by dry washing using corrosive gas.
[0004]
[Problem(s) to be Solved by the Invention] However, removal of the silicon natural oxidation film formed in the silicon layer front face fluoric acid system liquid and its steam -- easy -- being removable (reference, such as a ****** No. 502930 [62 to] official report) -- Removal of the metal natural oxidation film formed in the metal layer front face is very difficult. Control of a process is difficult, and the above-mentioned approach dry washing removes the metal natural oxidation film cannot remove only the natural oxidation film alternatively, either, and is expensive, and has a trouble of adsorption of the reaction component molecule to a damage [of a substrate] and substrate top etc. [of processing cost] Thus, the present condition is having not yet found the effective method of removing the metal natural oxidation film from a metal layer front face.
[0005] This invention is made in view of the above situations, it can remove alternatively the metal natural oxidation film formed in the front face of a metal layer, without making it corrode to a metal

layer, and aims at offering the washing approach on the front face of a substrate that neither the impurity to a substrate top nor adhesion of a resultant takes place.

[0006]

[Means for Solving the Problem] Use a sulfuric anhydride as a caustic agent, supply the steam of that sulfuric anhydride on the surface of a substrate, the metallic oxide and sulfuric anhydride which were put on the substrate front face in the shape of a thin film are made to react, and it was made to make a sulfate generate in this invention. Then, pure water is supplied on the surface of a substrate, and the sulfate adhering to a substrate front face is dissolved, and it removes from a substrate front face, and was made to dry a substrate front face after that. As for the above each process, especially desiccation process, it is desirable that it is made to carry out in an inert gas ambient atmosphere, and it is desirable to use the pure water which does not have dissolved oxygen ******** rare **** as pure water supplied to a substrate front face.

[0007] Here, when the sulfuric acid with which the front face of a metal layer contained water in the substrate covered with the metal oxide film is contacted, it will be corroded by the sulfuric acid to the metal layer not only a surface metal oxide film but under it. On the other hand, by the approach of this invention, since he is trying to supply the steam of a sulfuric anhydride on the surface of a substrate, a surface metallic oxide and a surface sulfuric anhydride react, only a metal oxide film is corroded, and the metal layer under it is not corroded. Moreover, a substrate does not receive a damage. And when a metallic oxide (M2O3) and a sulfuric anhydride (SO3) react directly, as shown in ** 1, a sulfate (M2 (SO4) 3) generates.

[0008]

[Formula 1]

$$M_2O_3 + 3SO_3 \longrightarrow M_2(SO_4)_3$$

[0009] By the sulfate generated by the reaction of a metallic oxide and a sulfuric anhydride being easy to dissolve in water, and supplying pure water to a substrate front face, it dissolves into pure water, a sulfate is removed from on a substrate, and impurities, such as the organic substance, are also flushed from a substrate front face with pure water. At this time, the pure water which does not have dissolved oxygen ******** rare **** is used, and a fear of the reconstititution of the metal oxide film being again carried out for the front face of the metal layer from which the metal oxide film was removed when it was made to perform desiccation processing on the front face of a substrate within the inert gas ambient atmosphere to a metal layer front face in response to the oxidation disappears.

[0010]

[Example] Hereafter, the suitable example of this invention is explained.

[0011] Drawing 1 is the outline sectional view showing one example of the configuration of the washing station used for enforcing the substrate surface washing approach concerning this invention. This washing station arranges the rotation support table 16 which lays a wafer in a top face and rotates in a horizontal plane in the chamber 10 which has the wafer taking-out inlet port 12 in which the closing motion shutter 14 was arranged, and is constituted. While free passage connection of the steamy feeder 18 of a sulfuric anhydride is made through the steam line 20, free passage connection of the nitrogen source of supply is made through gas piping 22 at the chamber 10. Moreover, the pure-water jet pipe 24 with which the injection tip was turned in the direction of the top face of the rotation support table 16 inside a chamber 10 is arranged by the chamber 10, and passage connection of the pure-water source of supply is made through water supply piping 26 at the pure-water jet pipe 24. Moreover, the effluent and the exhaust port 28 are formed in the pars basilaris ossis occipitalis of a chamber 10.

[0012] The equipment shown in drawing 1 is used, and as it is the following, washing processing on the front face of a substrate is performed. First, a substrate, for example, a wafer with metal electrode wiring, is carried in into a chamber 10 through the wafer taking-out inlet port 12, and the wafer taking-out inlet port 12 is blockaded with the closing motion shutter 14 after that. And inert gas, for example, nitrogen gas, is sent in through gas piping 22 from a nitrogen source of supply into a chamber 10, and feeding nitrogen gas is continued into a chamber 10 until a series of washing processings are completed,

and the inside of a chamber 10 is henceforth maintained at the inert gas ambient atmosphere in which oxygen does not exist. A steam line 20 is introduced for the steam of a sulfuric anhydride into the through chamber 10 with inactive carrier gas (nitrogen gas) from the steamy feeder 18 in this condition, and the steam of a sulfuric anhydride is supplied to the front face of a wafer with metal electrode wiring. The aluminum natural oxidation film (aluminum 2O3) which has covered with this processing the front face of the metal layer which forms metal electrode wiring on a wafer, for example, an aluminum layer, is corroded by the sulfuric anhydride, and as the direct reaction at that time shows to ** 2, an aluminum sulfate (aluminum2(SO4) 3) generates.

[0013]

[Formula 2]

$$Al_2O_3 + 3SO_3 \longrightarrow Al_2(SO_4)_3$$

[0014] In this case, generally, only the surface aluminum natural oxidation film is corroded and aluminum is not corroded to the aluminum layer under it (electrode wiring) so that it may be found also from being selected as a corrosion preventive to a sulfuric anhydride.

[0015] Next, the pure water which does not have through dissolved oxygen ******** rare **** in water supply piping 26 is supplied to a chamber 10 from a pure-water source of supply, and pure water is sprayed on the front face of the wafer by which installation immobilization is carried out on the rotation support table 16 from the pure-water jet pipe 24. An aluminum sulfate is removed from on a wafer together with the water which dissolves an aluminum sulfate into pure water (the solubility of the aluminum sulfate to water is 107.4g/100g), and flows down from a wafer front face by this processing. Moreover, the organic substance adhering to a wafer front face etc. is flushed at this time. And waste fluid is discharged out of a chamber 10 together with nitrogen gas from an effluent and an exhaust port 28.

[0016] After drying a wafer front face under nitrogen-gas-atmosphere mind and completing desiccation processing finally, continuing supplying nitrogen gas into a chamber 10, a wafer is taken out from a chamber 10 and a wafer is transported to a next processing room, for example, a metal membrane formation room, or a next etching processing room.

[0017] Drawing 2 is drawing for explaining the process in which the metal natural oxidation film is removed with the application of the substrate surface washing approach concerning this invention. Covering formation of the metal layer 32, for example, the aluminum layer, is carried out on the front face of an insulating layer 30, the aluminum natural oxidation film 34 is formed in the front face of the aluminum layer 32, and (a) of drawing 2 shows the condition that covering formation of the insulator layer 36 which has a through hole 38 on the aluminum layer 32 by which the front face was covered with the aluminum natural oxidation film 34 is carried out. If the metal layer of a two-layer eye is formed in the front face of an insulator layer 36, and a through hole 38 with the condition which showed in (a) of this drawing 2 , since it will produce un-arranging [which it is called increase of contact resistance etc.], the part corresponding to the formation part of a through hole 38 of the aluminum natural oxidation film 34 is removed using the approach concerning this above-mentioned invention. Thereby, as shown in (b) of drawing 2 , the front face of the aluminum layer 32 which the aluminum natural oxidation film is removed by the pars basilaris ossis occipitalis of the through hole 38 of an insulator layer 36, and adhesion of impurities, such as the organic substance, does not have in it, either is exposed. After changing into this condition, as shown in (c) of drawing 2 , the substrate to which the layer [1st] aluminum layer 32 and the aluminum layer 40 of a two-layer eye were directly connected through the through hole 38 is obtained by forming the aluminum layer 40 of a two-layer eye on an insulator layer 36.

[0018] moreover, although not illustrated, in carrying out etching processing of the metal layer by which covering formation was carried out on the surface of the insulating substrate, for example, the aluminum layer The aluminum natural oxidation film formed in the front face of the part which is not covered with the resist film of the aluminum layer covered with the resist film of a necessary pattern What is necessary is to etch the part which is not covered with the resist film of an aluminum layer after

removing using the approach concerning this above-mentioned invention, and just to make the resist film exfoliate from on an aluminum layer after etching. Thus, after removing the natural oxidation film, by carrying out etching processing of the aluminum layer, etching processing can be carried out to homogeneity. Moreover, after exfoliating the resist film from on an aluminum layer, the aluminum natural oxidation film which remains into the part covered with the resist film of the front face of an aluminum layer is removed using the approach of starting this invention again. Some flow charts of the device production process which used the approach concerning this invention for drawing 3 are shown.
[0019]
[Effect of the Invention] Since it is constituted and this invention acts as explained above, if the front face of a substrate is washed by the approach concerning this invention Only the metal natural oxidation film formed in the front face, without making a metal layer corrode is removed alternatively. This invention can greatly contribute to upgrading of a semiconductor device or an electron device, without there being no adhesion of impurities, such as the organic substance, and a resultant, and being able to obtain the pure metal layer front face which is not covered with the metal natural oxidation film, and a substrate receiving a damage, in case it is washing.

[Translation done.]

* NOTICES *

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TECHNICAL FIELD

[Industrial Application] This invention relates to the washing approach on the front face of a substrate of removing the metal natural oxidation film formed in the front face of the metal layer on a substrate from on a substrate, in production processes, such as a semiconductor device and an electron device.

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PRIOR ART

[Description of the Prior Art] In a semiconductor device or an electron device, the contact part with the electrode, the semiconductor device body, or other electrode wiring which transmit or take out the electrical signal from a component was called the contact section, and they are electrically connected through the contact hole and through hole which were formed in the insulator layer on a substrate. The ohmic nature from which the current-voltage characteristic serves as linear relation, low contact resistance, interface stability, good adhesion, etc. are required of this contact section. By the way, in the production process of a semiconductor device or an electron device, the natural oxidation film is easily formed into air, and it grows up to be the front face of the metal layer formed on the substrate. For example, the report that the saturation thickness of the natural oxidation film of the aluminum in a room temperature is 3nm is made.
[0003] Many above-mentioned demands are no longer filled except that the contact resistance in a device will increase, if the surface of metal of a semiconductor device, lower layer electrode wiring or a through hole, or a contact hole remains covered with the natural oxidation film. Furthermore, if the natural oxidation film is formed in the front face of a metal layer in the manufacture process of a semiconductor device or an electron device, a metaled etching reaction will be checked and it will become the cause of ununiformity processing. Therefore, in each phase of the production process of a semiconductor device or an electron device, if the natural oxidation film is formed in the front face of a metal layer, it is necessary to remove it completely from a metal layer front face. Conventionally, the metal natural oxidation film formed in the front face of a metal layer was removed by dry washing using corrosive gas.

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EFFECT OF THE INVENTION

[Effect of the Invention] Since it is constituted and this invention acts as explained above, if the front face of a substrate is washed by the approach concerning this invention Only the metal natural oxidation film formed in the front face, without making a metal layer corrode is removed alternatively. This invention can greatly contribute to upgrading of a semiconductor device or an electron device, without there being no adhesion of impurities, such as the organic substance, and a resultant, and being able to obtain the pure metal layer front face which is not covered with the metal natural oxidation film, and a substrate receiving a damage, in case it is washing.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, removal of the silicon natural oxidation film formed in the silicon layer front face fluoric acid system liquid and its steam -- easy -- being removable (reference, such as a ****** No. 502930 [62 to] official report) -- Removal of the metal natural oxidation film formed in the metal layer front face is very difficult. Control of a process is difficult, and the above-mentioned approach dry washing removes the metal natural oxidation film cannot remove only the natural oxidation film alternatively, either, and is expensive, and has a trouble of adsorption of the reaction component molecule to a damage [of a substrate] and substrate top etc. [of processing cost] Thus, the present condition is having not yet found the effective method of removing the metal natural oxidation film from a metal layer front face.
[0005] This invention is made in view of the above situations, it can remove alternatively the metal natural oxidation film formed in the front face of a metal layer, without making it corrode to a metal layer, and aims at offering the washing approach on the front face of a substrate that neither the impurity to a substrate top nor adhesion of a resultant takes place.

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MEANS

[Means for Solving the Problem] Use a sulfuric anhydride as a caustic agent, supply the steam of that sulfuric anhydride on the surface of a substrate, the metallic oxide and sulfuric anhydride which were put on the substrate front face in the shape of a thin film are made to react, and it was made to make a sulfate generate in this invention. Then, pure water is supplied on the surface of a substrate, and the sulfate adhering to a substrate front face is dissolved, and it removes from a substrate front face, and was made to dry a substrate front face after that. As for the above each process, especially desiccation process, it is desirable that it is made to carry out in an inert gas ambient atmosphere, and it is desirable to use the pure water which does not have dissolved oxygen ******** rare **** as pure water supplied to a substrate front face.
[0007] Here, when the sulfuric acid with which the front face of a metal layer contained water in the substrate covered with the metal oxide film is contacted, it will be corroded by the sulfuric acid to the metal layer not only a surface metal oxide film but under it. On the other hand, by the approach of this invention, since he is trying to supply the steam of a sulfuric anhydride on the surface of a substrate, a surface metallic oxide and a surface sulfuric anhydride react, only a metal oxide film is corroded, and the metal layer under it is not corroded. Moreover, a substrate does not receive a damage. And when a metallic oxide (M2O3) and a sulfuric anhydride (SO3) react directly, as shown in ** 1, a sulfate (M2 (SO4) 3) generates.
[0008]
[Formula 1]

$$M_2O_3 + 3SO_3 \longrightarrow M_2(SO_4)_3$$

[0009] By the sulfate generated by the reaction of a metallic oxide and a sulfuric anhydride being easy to dissolve in water, and supplying pure water to a substrate front face, it dissolves into pure water, a sulfate is removed from on a substrate, and impurities, such as the organic substance, are also flushed from a substrate front face with pure water. At this time, the pure water which does not have dissolved oxygen ******** rare **** is used, and a fear of the reconstitution of the metal oxide film being again carried out for the front face of the metal layer from which the metal oxide film was removed when it was made to perform desiccation processing on the front face of a substrate within the inert gas ambient atmosphere to a metal layer front face in response to the oxidation disappears.

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EXAMPLE

[Example] Hereafter, the suitable example of this invention is explained.
[0011] Drawing 1 is the outline sectional view showing one example of the configuration of the washing station used for enforcing the substrate surface washing approach concerning this invention. This washing station arranges the rotation support table 16 which lays a wafer in a top face and rotates in a horizontal plane in the chamber 10 which has the wafer taking-out inlet port 12 in which the closing motion shutter 14 was arranged, and is constituted. While free passage connection of the steamy feeder 18 of a sulfuric anhydride is made through the steam line 20, free passage connection of the nitrogen source of supply is made through gas piping 22 at the chamber 10. Moreover, the pure-water jet pipe 24 with which the injection tip was turned in the direction of the top face of the rotation support table 16 inside a chamber 10 is arranged by the chamber 10, and passage connection of the pure-water source of supply is made through water supply piping 26 at the pure-water jet pipe 24. Moreover, the effluent and the exhaust port 28 are formed in the pars basilaris ossis occipitalis of a chamber 10.
[0012] The equipment shown in drawing 1 is used, and as it is the following, washing processing on the front face of a substrate is performed. First, a substrate, for example, a wafer with metal electrode wiring, is carried in into a chamber 10 through the wafer taking-out inlet port 12, and the wafer taking-out inlet port 12 is blockaded with the closing motion shutter 14 after that. And inert gas, for example, nitrogen gas, is sent in through gas piping 22 from a nitrogen source of supply into a chamber 10, and feeding nitrogen gas is continued into a chamber 10 until a series of washing processings are completed, and the inside of a chamber 10 is henceforth maintained at the inert gas ambient atmosphere in which oxygen does not exist. A steam line 20 is introduced for the steam of a sulfuric anhydride into the through chamber 10 with inactive carrier gas (nitrogen gas) from the steamy feeder 18 in this condition, and the steam of a sulfuric anhydride is supplied to the front face of a wafer with metal electrode wiring. The aluminum natural oxidation film (aluminum 2O3) which has covered with this processing the front face of the metal layer which forms metal electrode wiring on a wafer, for example, an aluminum layer, is corroded by the sulfuric anhydride, and as the direct reaction at that time shows to ** 2, an aluminum sulfate (aluminum2(SO4) 3) generates.
[0013]
[Formula 2]

$$Al_2O_3 + 3SO_3 \longrightarrow Al_2(SO_4)_3$$

[0014] In this case, generally, only the surface aluminum natural oxidation film is corroded and aluminum is not corroded to the aluminum layer under it (electrode wiring) so that it may be found also from being selected as a corrosion preventive to a sulfuric anhydride.
[0015] Next, the pure water which does not have through dissolved oxygen ******** rare **** in water supply piping 26 is supplied to a chamber 10 from a pure-water source of supply, and pure water is sprayed on the front face of the wafer by which installation immobilization is carried out on the rotation support table 16 from the pure-water jet pipe 24. An aluminum sulfate is removed from on a wafer together with the water which dissolves an aluminum sulfate into pure water (the solubility of the

aluminum sulfate to water is 107.4g/100g), and flows down from a wafer front face by this processing. Moreover, the organic substance adhering to a wafer front face etc. is flushed at this time. And waste fluid is discharged out of a chamber 10 together with nitrogen gas from an effluent and an exhaust port 28.

[0016] After drying a wafer front face under nitrogen-gas-atmosphere mind and completing desiccation processing finally, continuing supplying nitrogen gas into a chamber 10, a wafer is taken out from a chamber 10 and a wafer is transported to a next processing room, for example, a metal membrane formation room, or a next etching processing room.

[0017] Drawing 2 is drawing for explaining the process in which the metal natural oxidation film is removed with the application of the substrate surface washing approach concerning this invention. Covering formation of the metal layer 32, for example, the aluminum layer, is carried out on the front face of an insulating layer 30, the aluminum natural oxidation film 34 is formed in the front face of the aluminum layer 32, and (a) of drawing 2 shows the condition that covering formation of the insulator layer 36 which has a through hole 38 on the aluminum layer 32 by which the front face was covered with the aluminum natural oxidation film 34 is carried out. If the metal layer of a two-layer eye is formed in the front face of an insulator layer 36, and a through hole 38 with the condition which showed in (a) of this drawing 2 , since it will produce un-arranging [which it is called increase of contact resistance etc.], the part corresponding to the formation part of a through hole 38 of the aluminum natural oxidation film 34 is removed using the approach concerning this above-mentioned invention. Thereby, as shown in (b) of drawing 2 , the front face of the aluminum layer 32 which the aluminum natural oxidation film is removed by the pars basilaris ossis occipitalis of the through hole 38 of an insulator layer 36, and adhesion of impurities, such as the organic substance, does not have in it, either is exposed. After changing into this condition, as shown in (c) of drawing 2 , the substrate to which the layer [1st] aluminum layer 32 and the aluminum layer 40 of a two-layer eye were directly connected through the through hole 38 is obtained by forming the aluminum layer 40 of a two-layer eye on an insulator layer 36.

[0018] moreover, although not illustrated, in carrying out etching processing of the metal layer by which covering formation was carried out on the surface of the insulating substrate, for example, the aluminum layer The aluminum natural oxidation film formed in the front face of the part which is not covered with the resist film of the aluminum layer covered with the resist film of a necessary pattern What is necessary is to etch the part which is not covered with the resist film of an aluminum layer after removing using the approach concerning this above-mentioned invention, and just to make the resist film exfoliate from on an aluminum layer after etching. Thus, after removing the natural oxidation film, by carrying out etching processing of the aluminum layer, etching processing can be carried out to homogeneity. Moreover, after exfoliating the resist film from on an aluminum layer, the aluminum natural oxidation film which remains into the part covered with the resist film of the front face of an aluminum layer is removed using the approach of starting this invention again. Some flow charts of the device production process which used the approach concerning this invention for drawing 3 are shown.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the outline sectional view showing one example of the configuration of the washing station used for enforcing the substrate surface washing approach concerning this invention.
[Drawing 2] some substrates for explaining the example of application of the substrate surface washing approach concerning this invention -- it is an enlarged vertical longitudinal sectional view.
[Drawing 3] It is the flow chart which shows some procedures of the device production process using the substrate surface washing approach concerning this invention.
[Description of Notations]
10 Chamber
16 Rotation Support Table
18 Steamy Feeder of Sulfuric Anhydride
22 Nitrogen Gas Piping
24 Pure-Water Jet Pipe

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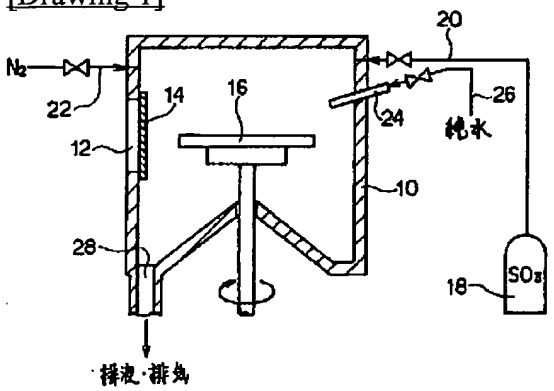
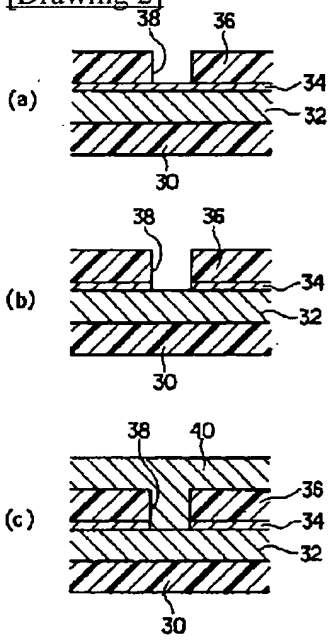
DRAWINGS

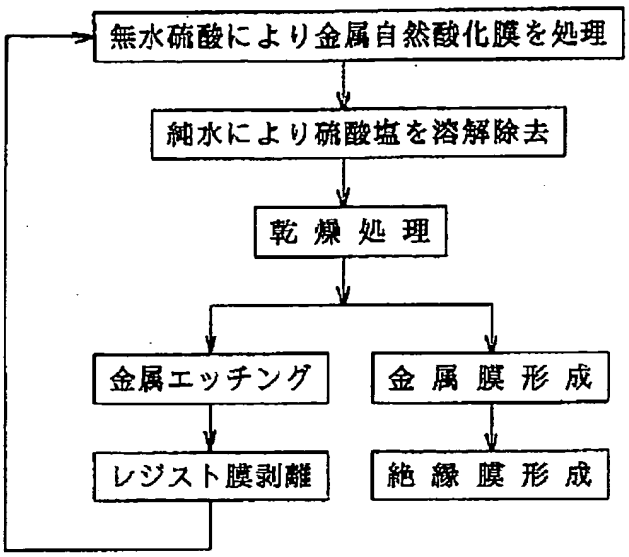
[Drawing 1]



[Drawing 2]



[Drawing 3]



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